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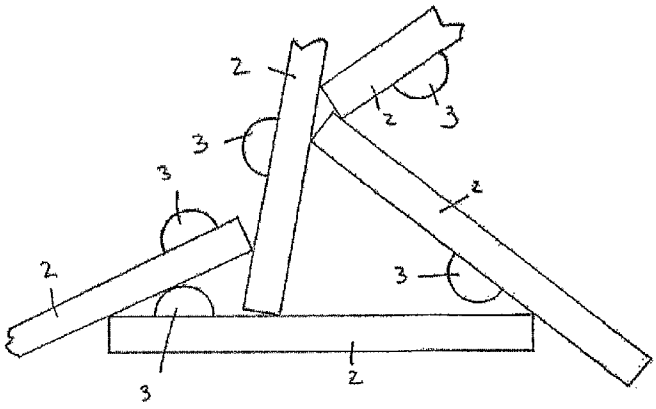
(54) Title: IMPROVED CATALYST



(57) Abstract: A catalyst (1) comprising a catalytic material (3) supported on a support (2), characterised in that the support (2) comprises particles predominantly having a maximum particle size of less than 1000 nm and an aspect ratio of greater than 2, and the. catalytic material (3) is mainly present in the form of discrete islands of catalytic material (3) supported on the support (2), with a substantial proportion of the islands of catalytic material (3) being separate and isolated from other islands of catalytic material (3). The islands of catalytic material (3) are separate and isolated from other islands of catalytic material (3) such that diffusion and growth of the islands of catalytic material (3) at elevated temperature is minimised or avoided.

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IMPROVED CATALYST

Field of the Invention

The present invention relates to an improved catalyst. The present invention particularly relates to an improved catalyst in which a catalytic material is supported on a support. The present invention also relates to methods for making such catalysts.

Background to the Invention

Catalysts are widely used in a large number of industries. Some examples of industries that utilise catalysts include oil refining (especially cracking and reforming), automotive manufacture (especially exhaust catalysts, such as three way catalysts), plastics manufacturing, production of synthesis gas, chemical synthesis processors, absorption and fuel cell manufacture.

A wide range of catalysts are of the type known as supported catalysts. In these catalysts, a catalytic material is supported on a support substrate. The support substrate may be in the form of powder, particles or monoliths. The support substrate is normally selected on the basis of the substrate being able to resist the conditions under which the catalyst is used. It will be appreciated that the conditions under which the catalyst is used may include one or more of elevated temperature, elevated pressure, and aggressive chemical environments. The support substrate may be relatively inert or it may itself have some catalytic activity. Support catalysts also include a catalytic material supported on the support substrate.

The catalytic activity of supported catalysts will primarily be a function of:

(a) The specific catalytic activity of the particular catalytic material supported on the support material;

(b) The amount of catalytic material supported on the support material; and

(c) The surface area of the catalytic material on the support material.

With regard to (a) above, it is know that some catalytic materials have greater catalytic activity (or a greater catalysing effect) for a particular reaction. For

example, noble metals are known to be effective at catalysing the oxidation of automotive exhaust gases.

With regard to (b) above, a higher loading of catalytic material on the support material should, all things otherwise being equal, increase the amount of catalytic material available to catalyse reactions. Similarly, with regard to (c) above, as it is the surface of the catalytic material that is involved in the catalysed reaction, a larger surface area of catalytic material should provide for an increased reaction rate.

Thus, it is expected that the best supported catalyst for any particular application would have the most catalytically active catalytic material present on the support material at as higher loading as possible and presenting the highest surface area as possible. However, in practice, a number of other factors must also be taken into consideration. For example, the most catalytically active material for a particular application may be prohibitively expensive. The supported catalyst may be difficult to manufacture, or it may degrade (i.e. lose its catalytic activity) over time. Degradation of catalytic performance may arise due to poisoning of the catalytic material, loss of catalytic material from the support (such as by leaching, erosion or abrasion) or by loss of surface area due to diffusion and growth of the catalytic material at elevated temperatures.

A number of workers have attempted to produce improved catalysts. Some of this are discussed below.

US Patent 6,706,902 to Sturmann et al (assigned to Bayer AG) describes the production of nano-scale precious metal particles on SiH-containing support materials. These catalysts are described as being useful in the catalytic oxidation of hydrocarbons, such as the oxidation of propene.

The catalysts described in Sturmann et al has precious metal particles present in a form such that more 50% of the precious metal particles have a diameter of less than 10nm. In this regard, Sturmann et al states that typically, only gold particles of less then 10nm are catalytically active (gold being the preferred precious metal described in Sturmann et al). To manufacture the catalyst of Sturmann et al, a support material which has SiH groups is brought into contact with at least one precious metal compound and/or precious metal particles for a time span of less than 2

hours. The support material is the immediately dried using spray drying or fluidised bed drying.

Although Sturmann et al makes a brief statement that the process can also be used advantageously with SiH-free support materials to generate metal particles and/or metal oxide particles in the lower nano-scale range, no support is proved for this statement. Indeed, claim 1 of Sturmann et al is limited to a reasonably complex support composition containing SiH-groups.

Preferred uses of the catalyst of Sturmann et al is in the gaseous phase reaction of oxygen with hydrocarbons in the presence of hydrogen. In this case, epoxides are selectively obtained from olefins, ketones from saturated secondary hydrocarbons, and alcohols from saturated tertiary hydrocarbons.

US Patent No. 6,746,597 in the name of Zhou et al (assigned to Hydrocarbon Technologies, Inc.) describes supported nanometer-sized catalytic crystal particle compositions of noble metals, wherein the exposed faces of the nanometer-sized catalyst particles comprise predominantly crystal planes of the (111) type.

Zhou et al states that a large number of chemical transformations are accomplished using heterogeneous catalysts with the active component of the catalysts is a metal, often deposited on a support material. An important class of catalysts are those which utilise noble metals including the platinum group of metals (platinum, palladium, rhodium, ruthenium, iridium and osmium) as well as silver, gold and rhenium. In comparison to other catalytic materials, noble metals often have a especially high activity and selectivity and are, therefore, frequently preferred over other catalyst materials.

Because of their ability to facilitate the dissociative absorption, surface reaction and recombination/desorption of hydrogen, noble metals can catalyse a wide range of commercially important reactions, particularly the transfer, reaction or activation of hydrogen. These reactions and associated processes include various hydrogenations and related reactions such as methanation, carbonylation, hydroformylation, reductive alkylation, amination, hydrosilation, ammonia synthesis, oil or fat hardening and the like. Noble metal catalysis is also particularly useful in

dehydrogenation reactions such as catalytic reforming, dehydrohalogenation reactions, steam reforming, partial oxidation and the production of gases including synthesis gas, hydrogen, carbon monoxide, carbon dioxide and the like. Noble metals are also used in important electrochemical processes such as fuel cell applications.

Despite their wide ranging effectiveness in catalytic chemical processes, Zhou et al states that noble metal catalysts have critical liabilities as the catalyst of choice for commercial chemical operations. Noble metals are extremely high cost and high catalyst attrition rates in given chemical process can negate the choice of noble metals as a preferred catalyst for that process. According to Zhou et al, their high cost also requires that their superior catalytic activity be sufficiently high compared to other catalyst choices to justify their use. To ameliorate the cost disadvantage, those skilled in the art can employ noble metal catalysts as small particles where by the overall efficiency of the catalyst is improved. This results in the greatest exposure of active noble metal surface areas for a given loading and offers the greatest noble metal utilisation. However, the high surface energy of the small particles tends to cause migration and agglomeration of the metal particles such that a catalyst which initially comprises very small particles and high noble metal surface area can lose surface area. Zhou et al states that improved methods are needed to prevent this migration and agglomeration of catalyst particles.

Zhou et al has discovered that supported nanometer scale noble metal particles containing a preponderance of (111) type of crystal phase upon the crystal face of the catalyst particles are especially effective catalysts. The support material for the noble metal catalyst is preferably a porous material such as porous alumina or carbon black. The particles of the invention described in Zhou et al preferably comprise noble metal particles of less then 5 nanometers, more preferably less then 2 nanometers. An important aspect of the invention of Zhou et al is the discovery that the most effective crystal phase of the noble metal particles useful in the selective reactions have a predominant exposure of the (111) type of crystal phase. Yet another important aspect of the invention of Zhou et al is the finding that the nanometer scale noble metal particles are anchored to the surface of the supporting substrate in a way that prevents this subsequent migration and agglomeration. Thus, the catalyst of Zhou et al includes the following advantages over other catalysts:

(a) A higher activity derived from the increased noble metal surface area of the extremely small crystallites containing the selective exposure of predominantly the (111) type of crystal phase upon the noble metal faces;

(b) Higher selectivity due to the selective exposure of the (111) type of crystal phase upon the noble metal crystal faces;

(c) An improved catalytic stability and life due to the anchoring of the noble metal crystallites. The strong anchoring of the crystallites to the substrate surface prevents a glomeration of metal particles into large structures, which would cause the disable high activity of the catalyst to be lost. Further, the strong anchoring substantially prevents the attrition of the active metal components into the surrounding liquid medium during use of the catalysts.

In order to form the catalysts of Zhou et al, a solution of a noble metal sold and a metallo-organic sequestering agent is formed. This solution is treated with a reducing agent. A catalyst support is then impregnated with the reduced noble metal solution and the impregnated support is dried. The catalyst is activated by reducing the dried impregnated support to yield the nanometer-sized noble metal catalysts having a preponderance of (111) type of crystal phase on the face of the noble metal particles. It seems that this process is required to obtain the strong anchoring of the noble metal crystallites to the substrate, as described in Zhou et al.

Zhou et al states that the noble metal particles are deposited on carbon or inorganic metal oxides support, minerals, polymeric materials and the like. Examples of noble metal catalyst supports are activated carbon, carbon black, fluoridated carbon, alumina, bentonite, clay, diatomaceous earth, zeolite, silica, zirconia, magnesia, titania, and the like, and also mixtures of those. The support is stated to be preferably a porous material having a surface area of more than 20 m^2/g. Any material that can serve as a useful support for a heterogenous catalyst may be used a support material for the catalyst of Zhou et al.

US 6,841,512 in the name of Fetcenko et al (assigned to Ovonic Battery Company, Inc.) describes an inexpensive catalytic material, especially non-

platinum and non-palladium catalytic materials, as well as an inexpensive method for manufacturing that catalyst material. The catalyst is described as being useful in fuel cells, particularly for facilitating hydrogen consumption in a fuel cell anode.

The catalyst described in Fetcenko et al comprises a metal particulate having a particle size less than about 100 angstroms (less than about 10nm) and support. The particulate may be affixed to the surface of the support. Alternately, the particulate may be partially or totally embedded into the support. The metal particulate is a plurality of metal particles. The catalytic metal particles are not limited to any particular shape, they may be regularly shaped or irregularly shaped. Examples of particle shapes (for the metal particles) include spherical, elongated, thread-like, and "sponge-like".

Fetcenko et al describes certain embodiments of the invention as having the metal particles situated in close proximity to one another so that the particulate has a high density and hence, a high density of catalytic activity. The particulate may have an average proximity that is preferably between about 2 and about 300 angstroms, and more preferably between 50 to about 100 angstroms.

Fetcenko et al states that generally, any support conventionally known in the art, capable of supporting and providing adequate dispersion of the particulate, may be used. The support is described as being one or more inorganic oxides, zeolites, fine grained oxides, course grained oxides or a mixture of fine grained and course grained oxides, a halide such as a chloride, a phosphide, or a nitride.

Although Fetcenko et al describes a wide range of possible supports, the only method of manufacturing the catalyst described in Fetcenko et al involves providing a hydrogen storage alloy and leaching that alloy such that the bulk of the alloy is converted to its equivalent metal oxide. However, parts of the alloy that are resistant to oxidation by the leaching solution remain as metal particles and it is these metal particles that form the metal particles sized less than 100 angstroms. Thus, Fetcenko et al states that by first formulating a hydrogen absorbing alloy material with an appropriate composition and then subjecting this alloy to a leaching process having the appropriate leaching conditions (i.e. time of leaching as well as temperature and pH of the leaching material), substantially the entire starting alloy may be oxidised to

form a highly catalytic material comprising a nickel and/or nickel alloy particulate embedded in an oxide support.

US Patent Application Publication No. 2005/0009696 in the name of Mao et al (assigned to 3M Innovative Properties Company), describes a supported catalyst having exceptionally small catalyst nanoparticles deposited on support particles in relatively high loading ratios. More particularly, the supported catalyst of Mao et al comprises catalyst metal nanoparticles having an average particle size of 3.0nm or less which are supported on support particles, wherein the weight of catalysts metal nanoparticles in the supported catalyst is 30% or more of the weight of the supported catalyst. According to Mao et al, the invention described therein provides a supported catalyst having exceptionally small catalyst nanoparticles deposited on support particles in relatively high loading ratios and methods of making such supported catalysts by depositing unprotected catalyst nanoparticles on support particles. As used in Mao et al, "unprotected", as used in reference to colloids of metal nanoparticles in organic or aqueous solvent means dispersed in weakly co-ordinating or non-coordinating solvent without protecting agents such as surfactants, polymers, or organic ligands.

Mao et al states that any suitable catalyst metal may be used. Typical catalyst metals are selected from platinum, palladium, ruthenium, rhodium, iridium, osmium, molybdenum, tungsten, iron, nickel and tin. Any suitable support particles may be used. Typical support particles are carbon, but may also be silica or other porus materials.

According to Mao et al, conventional methods of producing supported precious metal catalysts are typically unable to produce high loadings without concomitant increases in particle size. The increases in particle size limits the usefulness of the catalysts by reducing available surface area. Typical conventional methods include direct reduction of precious metals salts with reducing agents in the presence of a support, such as porous carbon or molecular sieve materials.

The method for making the catalyst described in Mao et al comprises the steps of providing a solution of metal chlorides of one or more catalyst metals in a solvent system containing at least one polyalcohol, forming a colloidal suspension of unprotected catalyst metal nanoparticles by raising the pH of the solution and heating

the solution, adding support particles to the colloidal suspension and depositing the unprotected catalyst metal nanoparticles on the support particles by lowering the pH of the suspension, typically to a pH of 6.5 or lower.

The catalysts described in Mao et al are stated to be useful in electro chemical cells such as fuel cells.

US Patent 6,857,431 in the name of Deevi et al (assigned to Philip Morris USA Inc.) describes nanocomposite copper-ceria catalysts for low temperature or near ambient oxidation of carbon monoxide, reduction of nitric oxide and/or conversion of hydrocarbons. Deevi et al describes a method for making nanocomposite copper-ceria catalysts which comprises combining ceria nanoparticles in an aqueous suspension with copper 2, 4-pentanedionate to form a slurry. The slurry is heated under an inert gas atmosphere of an oxygen-argon atmosphere at a temperature and for a time sufficient to cause decomposition of the copper 2, 4-pentanedionate to form copper nanoparticles and/or copper oxide nanoparticles are combined with the ceria nanoparticles. The so-formed product may be subsequently heat treated at a temperature of from 300-400°C.

The nanocomposite copper-ceria catalyst thus produced comprises copper oxide nanoparticles, copper nanoparticles or a mixture thereof combined with ceria nanoparticles. The nanocomposite copper-ceria catalyst may be less than about 500nm in size, preferably less than about 100nm in size, more preferably less than about 10nm in size and most preferably less than about 5nm in size.

The nanocomposite copper-ceria catalyst may be carried by catalyst support. Examples of the catalyst support include aluminum, alumina, titanium, titania, zirconia, magnesia, silica, silica gel, activated carbon, carbon fibers, carbon foam, and/or mixtures thereof. The nanocomposite copper-ceria catalyst can be deposited on the support catalyst or combined with catalyst support particles.

The catalyst particles described in Deevi et al are stated to be particularly useful in smoking articles, such as cigarettes. In particular, the catalyst particles can be mixed with the filter or formed into the filter paper or incorporated into the fibrous material of the cigarette filter portion.

International Patent Application No. WO 2005/002714, filed in the name of William Marsh Rice University, describes a process for making a porous catalyst. The process comprises providing an aqueous solution containing a

nanoparticle precursor, forming a composition containing nanoparticles, adding a first catalytic component or precursor thereof and a pore forming agent to the composition containing nanoparticles and allowing the first catalytic component, the pore forming agent, and the nanoparticles to form an organic-inorganic structure, removing water from the organic-inorganic structure, and removing the pore forming agent from the organic-inorganic structure so as to yield a porous catalyst.

In preferred embodiments, a metal oxide precursor is mixed with nanoparticles of a metal oxide support in a solution that contains a surfactant. The surfactant serves as a template for the metal oxide particles, which in turn support a self-assembled layer of the precursor salt species to the desired metal oxide layer. Once the nanoparticles, metal salt precursor and surfactant have self assembled, calcinations converts the salt species into a metal oxide layer and removes the surfactant to leave a porous structure.

The process of this patent application relies upon supramolecular templating synthesis of catalyst systems that is believed to entail the cooperative electrostatic and hydrogen bonding interactions among three components in order for self assembly to occur. The method allows the formation of a layer of metal oxide that is amorphous, rather than microcrystalline. The method also requires an ageing step to allow the self-templating of the components to occur. The examples of this patent show that precipitates are formed during the ageing step, which precipitates are washed, dried, ground into a fine powder and calcined. One outcome of such self-assembly methods is that the pore size distributions in the product are very sharp, since the pore size is primarily determined by the diameter of the surfactant micelles.

It is an object of the present invention to provide an alternative supported catalyst.

Brief Description of the Invention

In a first aspect, the present invention provides a catalyst comprising a catalytic material supported on a support, characterised in that the support comprises particles predominantly having a maximum particle size of less than 1000nm and an aspect ratio of greater than 2, and the catalytic material is mainly present in the form of discrete islands of catalytic material supported on the support, with a substantial proportion of the islands of catalytic material being separate and isolated from other islands of catalytic material. Suitably, the islands of catalytic material are separate

and isolated from other islands of catalytic material such that diffusion and growth of the islands of catalytic material at elevated temperature is minimised or avoided.

In a second aspect, the present invention provides a catalyst comprising a catalytic material supported on support particles, characterised in that the catalytic material is present at a volume percent of at least 1%, by volume of the catalyst, that the catalytic material is present in the form of discrete islands or particles on the support particles, and that the ratio of the length of the support particles to the width of the islands or particles of the catalytic material is at least 3:1.

In a third aspect, the present invention provides a catalyst comprising a catalytic material supported on support particles, characterised in that a ratio of surface area of support particles (calculated as if the support particles have zero porosity) to surface area of catalytic material is at least 2:1 and the catalytic material is present at a volume percent of at least 1%, by volume of the catalyst.

In a fourth aspect, the present invention provides a catalyst comprising a catalytic material supported on support particles, characterised in that the catalytic material is present in the form of discrete islands of material supported on the support particles and a substantial proportion of the support particles have only a single island of catalytic material thereon.

Preferably, the support material has an aspect ratio of greater than 2, suitably from 2-1000, more suitably from 2-500, even more suitably from 2 to 100, yet even more suitably from 5-50. In terms of maximising the space between islands of the catalytic material, higher aspect ratios for the support particles will increase the spacing. However, in practice, the upper limits of the aspect ratio of the support particles may be limited by the stability of the support particles. The support material is suitably in the form of needles, laths or platelets, most suitably needles or laths.

As used throughout this specification, the term "aspect ratio" when used in relation to the support particles, means the ratio of the largest dimension of the particles to the smallest dimension of the particles.

The support particles suitably have a maximum particle size of up to 1000nm. More suitably, the support particles have a maximum particle size that falls within the range of from about 20nm to about 500nm, more preferably from about 20nm to about 200nm. However, it will be appreciated that the support particles may include some particles that have a maximum particle size greater than these sizes

without departing from the scope of the present invention.

As mentioned above, suitably a substantial proportion of the islands of catalytic material are separated and isolated from other islands of catalytic material. For example, at least 50% of the islands of catalytic material (by number) may be isolated. More suitably, at least 60%, even more suitably at least 70%, yet more suitably at least 80%, of the islands of catalytic material may be isolated and not in contact with other islands of catalytic material.

More suitably, a substantial proportion of the support particles only have a single island of catalytic material supported thereon. For example, at least 50% of the support particles (by number) may have only have a single island of catalytic material supported thereon. More suitably, at least 60%, even more suitably at least 70%, yet more suitably at least 80%, of the support particles only have a single island of catalytic material supported thereon.

The islands of catalytic material are suitably sized such that a substantial proportion of the islands have a maximum diameter of less than 100nm, more suitably less than 20nm, even more suitably less than 10nm, yet even more suitably between 2 and 10nm.

In one embodiment, a least 50% of the islands of catalytic material are sized as set out in the immediately preceding paragraph. More suitably at least 60%, even more suitably at least 70%, yet even more suitably at least 80%, of the islands of catalytic material are sized as set out in the immediately preceding paragraph.

Suitably, the volume percent of catalytic material falls within the range of from about 1% to about 40%, more suitably from about 1% to about 30%, even more suitably from about 1% to about 20%, still even more suitably from about 5% to about 20%, yet even more suitably form about 10% to about 20%.

The ratio of the length of the support particles to the width of the islands or particles of the catalytic material is at least 3:1, more suitably at least 4:1, even more suitably from about 4:1 to about 100:1, most suitably from about 4:1 to 20:1. The support particles are suitably in the form of needles, laths or platelets. The support particles may also be branched particles. The branched particles may comprise a stable agglomeration of smaller particles, such as an agglomeration of plates or needles, having a branched structure.

Preferably, the ratio of surface area of support particles (calculated as if

the support particles have zero porosity) to surface area of catalytic material is at least 2:1, more preferably within the range of about 2:1 to about 100:1, even more preferably within the range from about 5:1 to about 100:1, yet even more preferably within the range from about 10:1 to about 25:1.

The catalyst material in accordance with the present invention may have a pore volume, following treatment at 500°C for 2 hours , for pores having a diameter falling within the range of 2 - 200nm, of from 0.50 – 2.10 cm^3/g, more preferably from 0.75 – 1.50 cm^3/g, even more preferably from 0.85 – 1.25 cm^3/g. The catalyst may have a pore volume, following treatment at 500°C for 2 hours, for pores having a diameter falling within the range of 10 – 200nm, of from 0.46 to 1.84 cm^3/g, more preferably from 0.69 to 1.38 cm^3/g, even more preferably from 0.78 to 1.15 cm^3/g. The catalyst may have a pore volume, following treatment at 500°C for 2 hours, for pores having a diameter falling within the range of 50 – 200nm, of from 0.20 to 0.8 cm^3/g, more preferably from 0.3 to 0.6 cm^3/g, even more preferably from 0.34 to 0.5 cm^3/g.

The catalyst material may have a pore volume, following treatment at 1000°C for 2 hours, for pores having a diameter falling within the range of 2 -200nm, of from 0.47 to 1.90 cm^3/g, more preferably from 0.71 to 1.43 cm^3/g, even more preferably from pore volume, even more preferably from 0.80 to 1.19 cm^3/g. The catalyst may have a pore volume, following treatment at 1000°C for 2 hours, for pores having a diameter falling within the range of from 10 – 200 nm, of from 0.45 to 182 cm^3/g, more preferably from 0.68 to 1.37 cm^3/g, even more preferably from 0.77 to 1.14 cm^3/g. The catalyst may have a pore volume, following treatment at 1000°C for 2 hours, for pores having a diameter falling within the range of 50 – 200nm, of from 0.15 – 0.6 cm^3/g, more preferably 0.22 – 0.45 cm^3/g, even more preferably from 0.25 to 0.38 cm^3/g.

The pore volume was calculated using the BJH method.

The support particles may comprise any suitable support material. Examples of suitable support materials include metal oxides, mixed metal oxides, silicate materials, carbon-based materials, polymeric materials, clay materials, zeolites, layered double hydroxide materials and the like. Some examples of suitable support materials include alumina, aluminium hydroxide, titania, zirconia, ceria, magnesia, mixed metal oxides including two or more of the previously mentioned

metal oxides, natural zeolites, synthetic zeolites, bentonite, montmorillinite, diatomaceous earth, carbon black, activated carbon, and the like. It will be appreciated that this list is not exhaustive. A precursor of the support particles may be used as a starting material. Such precursor is suitably in the form of solid particles that can be converted to the final support material either as part of the process for making the catalyst or after the catalyst has been made.

The support material is suitably resistant to the conditions to which the catalyst is exposed during use of the catalyst. For example, the support material should be resistant to one or more of elevated temperature, elevated pressure or reactive chemical environments. The most suitable support materials not only retain their physical and chemical integrity during use, they also exhibit stable morphology during use.

The catalytic material may comprise any suitable known catalytic material. Examples include noble metals, platinum group metals, catalytically active metals such as copper, nickel and cobalt, oxides of catalytically active metals, mixed metal oxides, complex metal oxides, perovskites and the like, and mixtures thereof. It will be appreciated that this list is not exhaustive and that the present invention encompasses any suitable catalytic material.

The catalytic material may include more than one catalytic material. For example, the catalytic material may include particles or regions of a platinum group metal and particles of a metal oxide or mixed oxide. The catalytic material may also include one type of catalytic material supporting another type of catalytic material. For example, the support material may support islands of a mixed metal oxide, which in turn may support one or more platinum group metals. The example of platinum group metals has been provided merely to exemplify this embodiment of the present invention and it will be appreciated that other catalytic materials besides platinum group metals fall within the scope of the present invention.

Where the catalytic material includes one or more complex oxides, the complex oxide produced by the present invention may be a single phase material or it may contain multiple phases. Where the complex oxide contains multiple phases, each phase is suitably of different composition to the other phases. One or more of the multiple phases may comprise an oxide of a single metal. Alternatively, one or more of the phases may comprise a complex metal oxide phase. The multiple phases may

also comprise one or more phases of an oxide of a single metal and one or more phases of a complex oxide.

In some embodiments, the catalytic material may include one or more complex metal oxides. Some suitable metal oxides that may be incorporated as the catalytic material in the present invention include complex oxides in which the metal species are evenly mixed throughout the metal oxide matrix. The complex metal oxide phase may be a perovskite. The crystal structure is that of the mineral 'Perovskite', chemical formula $CaTiO_3$. There are numerous different compounds with the perovskite crystal structure, including $SrTiO_3$, $YBa_2Cu_3O_x$ superconductor, and many La-based perovskites that are useful as catalysts and as electrodes in solid oxide fuel cells. La-based perovskites include $LaMnO_3$, $LaCoO_3$, $LaFeO_3$, and $LaGaO_3$

Various substitutions of different elements into the oxide lattice may be made to obtain desired physical properties. For example with perovskites, substitutions may be on the A site (e.g. Sr for La in $LaMnO_3$) and/or on the B site (e.g. Ni for Mn in $LaMnO_3$). Multiple elemental substitutions on either or both sites can be made to further tailor physical properties for specific applications. For example, a perovskite composition $(Ln_{0.2}La_{0.4}Nd_{0.2}Ca_{0.2})(Mn_{0.9}Mg_{0.1})O_3$, where Ln is approximately $La_{0.598}Nd_{0.184}Pr_{0.81}Ce_{0.131}Ca_{0.002}Sr_{0.004}$, is described in US patent 5,932,146 as being useful for solid oxide fuel cell electrodes.

The complex oxide material may include an oxide composition represented by the general formula:

$$A_{1-x}B_xMO_3$$

wherein

A is a mixture of lanthanide elements;

B is a divalent or monovalent cation;

M is an element or mixture of elements selected from the group consisting of elements of an atomic number from 22 to 32, 40 to 51, and 73 to 83; and

x is a number in the range $0.1 \leq x \leq 0.5$.

Another family of metal oxides that may be used as the catalytic material in the

present invention are metal oxides incorporating cerium. Oxides containing cerium and zirconium are particularly useful for automobile catalysts. These oxides may be expressed as $Ce_aZr_bX_cO_d$, where X is an element or a mixture of elements selected form the group consisting of elements of an atomic number of 22 to 32, 40 to 51, and 73 to 83.

The present inventors have found that the combination of the size and aspect ratio of the support particles, together with the size and distribution of the catalytic material thereon, results in more isolated islands or particles of catalytic material for a given volume fraction of islands or particles of catalytic material. Another aspect of the invention allows a much higher volume fraction of islands or particles of catalytic material to be incorporated onto the support for a given average particle-particle distance when using the combination of support and catalytic material outlined in the present invention. This may result in the relative isolation of the islands of catalytic material supported on the support particles from other islands of catalytic material, allows sufficiently high loading of the catalytic material onto the support to provide good catalytic activity for the catalyst whilst also minimising or avoiding diffusion or growth of the islands of catalytic material into larger regions of catalytic material if the catalyst is exposed to elevated temperatures. Thus, the catalyst of the present invention provides a catalyst having good levels of catalytic activity and exceptional resistance to loss of surface area of the catalytic material at elevated temperatures, which would otherwise lead to a loss of catalytic activity. Furthermore, in embodiments of the invention where the islands of catalytic material are sized such that a substantial proportion of are less then 20nm, high surface areas of catalytic material are also obtained which improves the catalytic activity of the catalysts.

In preferred forms, the catalyst of the present invention includes substantial porosity, particularly arising from pores having pore diameters between 7nm and 100nm. Porosity in the catalyst, especially in this size range, is desirable. In particular, the porosity of the catalyst in accordance with some embodiments of the present invention allows for good diffusion of the reactive gases or fluids into the catalyst and also promotes thermal stability of the catalyst.

In use, the catalyst will typically comprise a bulk mixture of the individual particles of the catalyst. The catalyst particles may be used in the form of a

bed. Alternatively, the catalyst particles may themselves be supported on a larger support, such as a monolith, a honeycomb support, or on macroscopic particles, suitably sized above 500 micrometres. As a further alternative, the catalyst particles may be bonded together to make larger particles or tablets or shapes. Any binders known to be suitable may be used in this regard.

As the catalyst, in use, will comprise a mixture of many catalyst particles, it will be understood that a proportion of the catalyst particles, preferably a minor proportion, may have properties that do not fall within the catalyst particles described herein. Provided that a substantial proportion of the catalyst particles, such as 50% of the catalyst particles (calculated by number), fall within the scope of the invention, the advantageous features arising from the invention are likely to be observed. Thus, the present invention encompasses catalysts in which a substantial proportion of the catalyst particles are as described herein.

The present invention also provides a method for preparing a catalyst including preparing a mixture of support particles predominantly having a maximum particle size of less than 1000nm and an aspect ratio of greater than 2 with one or more precursors of a catalytic material and treating the mixture to form a catalyst in which the catalytic material is mainly present in the form of discrete islands of catalytic material supported on the support particles, with a substantial proportion of the islands of catalytic material being separate and isolated from other islands of catalytic material such that diffusion and growth of the islands of catalytic material at elevated temperature is minimised or avoided.

The method may involve dispersing the support particles in a solution having pH that promotes dispersion and minimises aggregation of the support particles, followed by mixing that dispersion with a solution or mixture containing the one or more precursors of the catalytic material. The ideal pH of the solution in which the support particles are dispersed is dependent upon the type of particles being dispersed in the solution. It will be understood that the support particles should not be detrimentally affected by the preparation conditions used. For example, the particles should not undesirably dissolve under the pH conditions used (or, to put it another way, the pH conditions should be selected such that dissolution of the support particles is minimal). It has been found by the present inventors that the step of dispersing the support particles in the solution prior to mixing with the one or more

precursors of the catalytic material tends to result in a better distribution of catalytic material on the support particles with less aggregation of the support particles.

The dispersion step may result in the particles becoming monodispersed (i.e. agglomerates of the particles largely break up into individual particles). However, in some instances, it may be desirable to avoid monodispersion of the particles. An example where monodispersion could be avoided involves the use of branched particles that comprise a branched aggregate of particles. The branched particles may provide desirable porosity and surface area properties and thus it may be useful to disperse those particles without causing the aggregates of smaller particles to break down.

In one embodiment, the method of the present invention involves a modified form of method described in US Patent No. 6,752,979 in the name of the present applicants. In this patent, a solution containing one or more metal cations is mixed with a surfactant material such that micelles are formed. This mixture is then heated to form metal oxide particles. The entire contents of US Patent No. 6,752,979 are expressly incorporated herein by cross reference.

The method of the present invention may, in one embodiment, include modifying the method described in US Patent No. 6,752,979 by adding particles of the support material to the mixture of metal cation solution and surfactant, followed by heating to thereby form metal oxide supported on the particles of support material. The particles of support material may be added to the metal cation solution before adding the surfactant, or added after the solution and surfactant and solution are mixed. Pore forming particles may also be added, as described in our co-pending International Patent Application number PCT/AU2005/000081, the entire contents of which are herein incorporated by cross reference.

In other embodiments of the method of the present invention, the catalytic material is a complex oxide that may be produced utilizing a polymer-complex method, a co-precipitation method, a sol-gel method, a thermal evaporative method, a hydrothermal method or any other suitable method or combination thereof with those methods modified by adding particles of the support material thereto. Examples of such methods are given in US Patent No. 6,139,816 (Liu et al), US Patent No. 5,879,715 (Higgens et al), US Patent No. 5,770,172 (Linehan et al), US Patent No. 5,698,483 (Ong et al), US Patent No. 6,328,947 (Monden et al), US Patent

No. 5,778,950 (Imamura et al) and US Patent Application No. 2005/0008777 (McCleskey et al) the entire disclosure of the above referenced patents and patent applications are herein incorporated by cross-reference.

Other methods may also be used to form the catalyst. For example, if the catalytic material is a metal, a supported metal oxide phase supported on the support material may be prepared and that metal oxide phase subsequently subjected to a reduction process to form the metal.

Other methods for forming a metal supported on the support material may include sputtering, chemical vapour deposition, and the like.

The catalyst of the present invention may have a composition that various widely. The catalytic material may be chosen from a vast number of known catalytically active materials. The support material may be selected from a vast number of known catalyst support materials. The catalyst may be used in any application where a supported catalyst can be used. Examples include heavy oil hydro refining, reforming, hydrocarbon cracking, decomposition of nitrogen oxides, isomerization catalysts, dehydrogenation, hydrogenation, steam reforming, production of synthesis gas, desulphurisation, reductive amination processes, ammonia production, ammonia oxidation, oxidative dehydrogenation, hydrocracking, steam reforming of methane, reduction of sulphur oxides to sulphur, photocatalysts, polymerization catalysts, gas phase epoxidation, treatment of automotive exhaust gases, fuel cell manufacture, etc. This list is not exhaustive.

In order to exemplify some embodiments of the present invention, the following examples of some catalysts in accordance with the present invention are provided:

a) a catalyst having dehydrogenation and hydrogenation properties and comprise zeolites or porous oxides of Al, Si, Ti, Zr, Nb, Mg and/or Zn, carrying at least one hydrogenation metal selected from Ni, Co, Cu, Fe, Pd, Pt, Ru, Rh or combinations thereof.

b) catalysts having a combination of oxides of metals of subgroup VII with aluminum oxide on support materials made from silicon and titanium oxides, which may be used to prepare surfactant alcohols by dimerization of olefin mixtures, derivatization to give primary alcohols, and c) optional subsequent alkoxylation.

c) a catalyst which comprises at least one transition metal of group VIII

of the Periodic Table of the Elements, preferably palladium, used for producing β-ketoenol esters.

d) hydrogenation catalysts, such as metals of subgroup VIII of the Periodic Table of the Elements, which metals can be applied to support materials, such as active carbon or oxides of aluminum, of silicon or of other materials. These catalysts include supported catalysts based on nickel, palladium and/or platinum

e) at least one multimetal oxide active composition as described in US patent no 6,888,024, which can be used in for heterogeneously catalyzed partial gas phase oxidation of propene to acrylic acid.

f) supported palladium catalysts used for hydrogenation of terephthalic acid.

g) A hydrogenation catalyst , for the hydrogenation of maleic anhydride and its derivatives to THF (tetrahydrofuran) or its derivatives, which catalyst comprises copper oxide and at least one further metal or compound thereof, preferably an oxide, selected from the group consisting of Al, Si, Zn, La, Ce, the elements of groups IIIA to VIIIA and the elements of groups IA and IIA. The further metal oxide may be selected from the group consisting of silicon dioxide, zinc oxide, aluminum oxide, zirconium oxide and titanium dioxide. Suitably, the catalyst is selected from among copper oxide/aluminum oxide mixtures and copper oxide/zinc oxide/aluminum oxide mixtures.

h) catalysts that include transition metal compounds, in particular those of transition groups VI to VIII of the Periodic Table of the Elements, used in a process for preparing propene and, if desired, 1-butene by metathesis of olefins. Examples of such catalysts are Re_2O_7/Al_2O_3,. MoO_3 and CoO on Al_2O_3, WO_3SiO_2, WO_3SiO_2 and MgO. The support may be Al_2O_3, SiO_2, Fe_2O_3, or mixtures thereof such as SiO_2/Al_2O_3, $B_2O_3/SiO_2/Al_2O_3$ or Fe_2O_3/Al_2O_3.

i) isomerization catalysts, such as noble metal compounds on a support. Examples include RuO_3 on an inorganic support such as SiO_2, Al_2O_3 or TiO_2 or mixed supports, mixed catalysts comprising magnesium oxide, zirconium oxide and an alkali metal oxide on an inorganic support, palladium catalysts, for example on Al_2O_3 as support.

j) Catalysts used for the oxidation of propene to acrylic acid , such as multimetal oxide materials which generally contain heavy metal molybdates as main

component and compounds of various elements as promoters. Catalysts comprising an active phase of a multimetal oxide material for the preparation of .alpha.,.beta.-monoethylenically unsaturated aldehydes and/or carboxylic acids by gas-phase oxidation of an alkane, alkanol, alkene and/or alkenal of 3 to 6 carbon atoms are described, for example, in EP 0 000 835, EP 0 575 897, DE 198 55 913, U.S. Pat. No. 5,276,178, DE 30 06 894, U.S. Pat. No. 5,198,581, WO 98/24746, U.S. Pat. No. 4,438,217 and EP 0 807 465.

k) Catalysts which comprise noble metals and are suitable for catalyzing the reaction of hydrogen and oxygen to form hydrogen peroxide, including catalysts whose active component comprises at least one metal of the platinum group, in particular palladium or combinations of palladium and platinum. If desired, such catalysts may further comprise additional metals such as rhodium, iridium, osmium, ruthenium, rhenium, gold, copper, cobalt, tungsten, molybdenum, holmium, tin. The active composition of the catalysts is preferably applied to a support.

l) a catalyst which comprises a catalytically active amount of at least one oxygen-containing molybdenum and/or tungsten compound on an oxidic support material, used to produce polytetrahydrofuran.

m)A catalyst for the preparation of acrylic acid by heterogeneously catalyzed gas-phase oxidation of propane with molecular oxygen at elevated temperatures over at least one multimetal oxide material, as described in US patent no 6,867,328.

n) A hydrogenation catalyst comprising, as catalytically effective component, a composition including (a) iron or a compound based on iron or a mixture thereof; (b) a promoter based on 2, 3, 4 or 5 elements selected from the group consisting of aluminum, silicon, zirconium, titanium and vanadium, (c) a compound based on an alkali and/or alkaline earth metal, and (d) manganese. Examples of support materials are porous oxides such as aluminum oxide, silicon dioxide, alumosilicates, lanthanum oxide, titanium dioxide, zirconium dioxide, magnesium oxide, zinc oxide.

o) A catalyst used in the oxidation of aromatic hydrocarbons to carboxylic acids or carboxylic anhydrides. The catalyst includes multimetal oxides containing Ag, a metal selected from the group consisting of Li, Na, K, Rb, Cs, Ti, Mg, Ca, Sr, Ba, Cu, Zn, Cd, Pb, Cr, Au, Al, Fe, Co, Ni and/or Mo,

p) catalysts which consist of alkali metal oxides on catalyst supports, used in a process for preparing 2-cyclopentenones by converting 2- or 3-hexene-1,6-dicarboxylic acids or their esters.

q) Multimetal oxide materials containing molybdenum, vanadium, antimony, one or more of the elements W, Nb, Ta, Cr and Ce and nickel and, if required, one or more of the elements Cu, Zn, Co, Fe, Cd, Mn, Mg, Ca, Sr and Ba and having a 2-component structure, used for the gas-phase catalytic oxidative preparation of acrylic acid.

r) a catalyst comprising cobalt oxide and also an oxide of alkali metals, alkaline earth metals, rare earths or scandium or yttrium used in a process for preparing linear triamino compounds by reacting 1,3,6-tricyanohexane.

s) cobalt catalysts comprising magnesium oxide used in a process for hydrogenating nitrites.

t) a catalyst comprising cobalt and optionally, in addition, nickel and also at least one further doping metal on a particulate support material for use in a process for preparing primary amines by hydrogenating nitrites in the presence of the catalyst, as described in US 6,790,996.

u) a catalyst which comprises an inorganic, TiO_2 -containing support and, as active component, copper or a mixture of copper with at least one metal selected from the group consisting of zinc, aluminum, cerium, nobel metals and metals of transition group VIII

v) Supported oxidic catalysts suitable as catalysts for use in the preparation of phthalic anhydride by gas-phase oxidation of o-xylene or naphthalene. The supports comprise a silicate, silicon carbide, porcelain, aluminum oxide, magnesium oxide, tin dioxide, rutile, aluminum silicate, magnesium silicate (steatite), zirconium silicate or cerium silicate or mixtures thereof. Catalytically active constituents are generally titanium dioxide, particularly in the form of its anatase modification, together with vanadium pentoxide. In addition, the catalytically active composition may further comprise small amounts of many other oxidic compounds which act as promoters to influence the activity and selectivity of the catalyst, for example by reducing or increasing its activity. Examples of such promoters are alkali metal oxides, thallium(I) oxide, aluminum oxide, zirconium oxide, iron oxide, nickel oxide, cobalt oxide, manganese oxide, tin oxide, silver oxide, copper oxide, chromium

oxide, molybdenum oxide, tungsten oxide, iridium oxide, tantalum oxide, niobium oxide, arsenic oxide, antimony oxide, cerium oxide and phosphorus pentoxide.

w) hydrogenation catalysts that contain, as active components, elements selected from the group consisting of copper, silver, gold, iron, cobalt, nickel, rhenium, ruthenium, rhodium, palladium, osmium, iridium, platinum, chromium, molybdenum and tungsten, in each case in metallic form (eg. as Ra catalyst, oxidation state 0) or in the form of compounds, such as oxides, which are reduced to the corresponding metal under the process conditions, which may be used in a process for the preparation of tetrahydrogeraniol. Particularly preferred catalysts are those with Co, Ni, Cu, Ru, Pd and/or Pt as active components.

x) a Pt/ZnO catalyst used in a process for the selective liquid phase hydrogenation of carbonyl compounds to give the corresponding alcohols. Suitable supporting materials include all usual supporting materials, for example, .gamma.-Al_2O_3,.alpha.-Al_2O_3, SiO_2, TiO_2, ZrO_2,

y) an SiO.sub.2 -supported catalyst, which contains 0.1 to 10% by weight of Ir, Pt, Rh or Ru as the active component and is doped with 0.01 to 10% by weight tin, lead or germanium, used in the hydrogenation of citral.

z) catalysts for the decomposition of N20, including binary oxides such as MgO, NiO, ZnO, Cr_2O_3, TiO_2, WO_x, SrO, CuO/Cu_2O, Al_2O_3, Se_2O_3, MnO_2 or V_2O_5, if desired doped with metal oxides, lanthanide complexes such as La_2NiO_4, La_2CuO_4, Nd_2CuO_4 and multinary oxide compounds thereof, spinels, ternary perovskites, and also oxidic systems such as CuO--ZuO--Al_2O_3.CoO--MgO, CoO--La_2O_3, CO--ZnO, NiO--MoO_3 or metals such as Ni, Pd, Pt, Cu, Ag.

aa) catalysts for preparing secondary amines from primary amines, including. Ni--Cu--Cr_2O_3, Co--Cu--Cr_2O_3, the catalyst composition, having at least one element or at least one compound of an element of groups VIII and IB of the Periodic Table of the Elements, i.e. from the group consisting of Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag and Au,

ba) Co- and/or Ni-containing catalystsfor use in reductive amination

ca) catalysts comprising Pt/Sn as active component on a Zn spinel support for the dehydrogenation of small hydrocarbon molecules such as isobutane using steam as diluent

ca) Pt/Sn/Cs/Al_2 O_3 catalysts for the dehydrogenation of hydrocarbons

using steam dilution

da) catalysts based on mixed oxides of magnesium and aluminum and further comprising a noble metal of group VIII, a metal of group IVa and, if desired, an alkali metal of group Ia, of the Periodic Table of the Elements for the dehydrogenation of, for example, a gas mixture.

ea) dehydrogenation catalysts having a bimodal pore radius distribution and comprising a) zirconium dioxide, b) aluminum oxide, silicon dioxide and/or titanium dioxide and c) at least one element of main group I or II, an element of transition group III, an element of transition group VIII, of the Periodic Table of the Elements, lanthanum and/or tin. Such catalysts may be used in the dehydrogenation of C_2 -C_{16} –hydrocarbons.

fa) catalysts used for the preparation of maleic anhydride by heterogeneously catalyzed gas-phase oxidation. Such catalysts include oxidic multicomponent catalysts based on the oxides of vanadium and phosphorus (so-called V--P--O catalysts), for example (VO).sub.2 P.sub.2 O.sub.7. These catalysts may be mixed with promoters, for example zinc, zirconium, bismuth, antimony, tin, nickel, cobalt, iron, chromium, manganese and/or molybdenum. On use of benzene as starting compound, it is also possible to employ catalysts based on the oxides of vanadium and molybdenum.

ga) a catalyst that comprises palladium on an inert support for making hydrogen peroxide in which hydrogen and oxygen.

ha) catalysts used for the catalytic gas-phase oxidation of aromatic hydrocarbons such as benzene, the xylenes, naphthalene, toluene or durene. The catalytically active species is on a support material which is generally inert under the reaction conditions, e.g. quartz (SiO_2), porcelain, magnesium oxide, tin dioxide, silicon carbide, rutile, alumina, aluminum silicate, magnesium silicate (steatite), zirconium silicate or cerium silicate or a mixture of these support materials. The catalytically active constituents of the catalysts are generally titanium dioxide in the form of its anatase modification plus vanadium pentoxide. In addition, the catalytically active composition may further comprise small amounts of many other oxidic compounds which, as promoters.

ia) a catalyst comprising as active metal ruthenium alone or together with a least one metal from transition group I or VII of the Periodic Table, applied to a

support. The support comprises activated carbon, silicon carbide, alumina, silica, titanium dioxide, zirconium oxide, magnesium oxide, zinc oxide or a mixture of two or more thereof. The catalyst may be used in a process for hydrogenating pyridine, an alkylpyridine or a mixture of two or more thereof by contacting pyridine or the alkylpyridine or the mixture of two or more thereof with a hydrogen-containing gas at a temperature in the range of 50 to 120.degree. C. in the presence of the catalyst.

ja) supported catalysts comprising ceria and titania, used for decomposition of nitrogen oxides.

ka) catalyst for use on a diesel particulate filter comprising platinum and a cerium oxide

la) an exhaust gas catalyst comprising an oxide mixture having praseodymium and cerium, with zirconium and yttrium being added to the oxide mixture. The catalyst also includes one or more metals including palladium, platinum, or rhodium added to the oxide mixture

ma) an exhaust gas purification catalytic material containing: (a) a mixed oxide containing Ce and Zr for storing and releasing oxygen; and (b) a precious metal catalyst made of one or more kinds of precious metals.

na) iridium oxide based catalysts for use as anode catalysts in PEM water electrolysis. The catalyst may include iridium oxide (IrO_2) and optionally ruthenium oxide (RuO_2) in combination with a high surface area inorganic oxide (for example TiO_2, $A1_2O_3$, ZrO_2 and mixtures thereof).

oa) samarium oxide catalyst used in the isomerized synthesis with mixed CO and H_2 feed stream to obtain isomerized C_4 hydrocarbon product.

pa) a composite metallic oxide composed of active components (Mo, V and Cu), stabilizer (at least Sb and Ti) and a composite oxide of Ni, Fe, Si, Al, alkali metal and alkali-earth metal. The catalyst is useful for selective oxidation of unsaturated aldehydes, to obtain acrylic acid or methyl acrylic acid.

qa) A composite titanium oxide-silicon oxide

catalyst for synthesizing phenyl oxalate by ester exchange

ra) A carried MoO_3 catalyst for synthesizing phenyl oxalate by an ester exchange reaction.

sa) A catalyst for gasoline desulfurization that contains manganese oxide, silica oxide, alumina oxide, and nickel oxide.

ta) An Mg/Al mixed oxide catalyst for catalytic conversion of alkylene carbonate,

ua) A composite oxide catalyst for the oxidation of an olefin containing Mo and Bi , as described in EP1449579

va) a vanadium/titania-based catalyst for removing nitrogen oxides.

wa) Lanthanide-promoted rhodium-containing supported catalysts that are active for catalysing the production of synthesis gas from methane.

xa) cobalt-containing catalysts suitable for use in Fischer-Tropsch synthesis.

ya) an Mn/Al oxide catalyst for use in hydrogenation reactions, such as the conversion of methyl benzoate gas phase hydrogenation reaction

za) An exhaust gas purifying catalyst which contains a composite oxide having a perovskite structure represented by the general formula (1): $A_{1-x}A'_xB_{1-y-z}B'_yPt_zO_3$ wherein A represents at least one element selected from rare-earth elements and essentially including one or more rare-earth elements each having a valence of 3 as the only valence; A' represents at least one element selected from alkaline earth metals and Ag; B represents at least one element selected from Fe, Mn, and Al; B' represents at least one element selected from transition elements excluding Pt, Fe, Mn, Co, and the rare-earth elements; and x, y, and z are atomic ratios satisfying the following relations: $0 < x <= 0.5$, $0 <= y < 0.5$, and $0 < z <= 0.5$.

Ba) Catalyst for treating exhaust gases that include a catalytically active composite of alumina, an oxide of chromium and/or tungsten, calcium, strontium, barium, silicon and/or tin oxide and, optionally, zirconium oxide and a platinum group metal component incorporated in the composite.

bb) a catalyst for the reduction of nitrogen oxides comprising a support of inert refractory material carrying a thermally stable ThO_2 or ZrO_2 and deposited thereon a coating of a catalytically active metal such as palladium.

bc) a catalyst having a copper component, wherein at least 50 wt. % of the copper component is in the form of a copper oxide, aluminum oxide-spinel, which catalyst is useful for generating hydrogen in a fuel cell.

bd) A catalyst for controlling NO_x emissions during fluidised catalytic cracking that includes an acidic oxide support, cerium oxide, a lanthanide oxide other than ceria (such as praseodymium oxide), and, optionally, an oxide of a metal

from Groups Ib and IIb such as copper, silver and zinc.

be) A selective catalytic material used in a method for selective oxidation of carbon monoxide in the presence of hydrocarbons. The catalyst contains rhodium and a bismuth component either as a supported catalytic material dispersed on a refractory inorganic oxide support.

bf) supported nickel catalysts for use in various applications, such as hydrogenation and desulfurization.

bg) A catalyst composition disposed on a carrier comprising a mixture of (a) a composite of a cerium component, a zirconium component and a samarium component, (b) a catalytically effective amount of at least one precious metal component and (c) a refractory metal oxide support, for simultaneously catalyzing the oxidation of hydrocarbons and carbon monoxide and the reduction of nitrogen oxides. This can be used as a three way automotive exhaust catalyst.

bh) A catalyst suitable for the treatment of automotive engine exhaust containing a catalytic material such as one or more of platinum, rhodium and palladium dispersed on an activated alumina support, and an oxygen storage component which is an intimately mixed oxide of ceria and praseodymia.

bi) Catalysts comprising a major amount of the oxides of a first metal selected from copper or zinc, a second metal selected from chromium, molybdenum, tungsten and vanadium, and optionally, a minor amount of the oxide of a promoter metal selected from the group consisting of manganese, barium, zinc, nickel, cobalt, cadmium, iron and any combination thereof. The catalyst may be used in hydrogenation processes.

bj) A catalyst composition containing one or more binary oxides of palladium and rare earth metal such as Ce, La, Nd, Pr and/or Sm. The catalyst composition is used for the catalytic combustion of gaseous combustion mixtures of oxygen and carbonaceous fuels such as methane.

bk) A catalyst for treating gas streams which contain halogenated organic compounds, non-halogenated organic compounds, carbon monoxide or mixtures thereof which comprises at least one platinum group metal, zirconium oxide and at least one oxide of manganese, cerium or cobalt.

bl) Oxidation catalyst compositions-include a catalytic material containing ceria-and alumina and optionally, platinum or palladium.

bm) A supported catalyst including a praseodymium-palladium oxide compound for oxidation of combustion mixtures comprising oxygen (e.g., air) and gaseous carbonaceous fuels such as methane.

It will be appreciated that the above examples of catalysts and uses of such catalysts are provided for the purposes of illustration only and the present invention should not in any way be considered to be limited to the particular examples provided. The person skilled in this art will recognise that the present invention is widely applicable to the catalyst art and it may be used in respect of a very wide range of catalysts for use in a very wide range of applications.

As will be readily understood by the person skilled in the art, the support material and the catalytic material should be chosen such that they do not adversely interact with each other. Adverse interactions that should be avoided include poisoning of the catalytic material by the support and loss of integrity of the support due to interaction with the catalytic material.

The present invention also encompasses using support particles that have been coated with a coating, such as a coating to improve the bond between the support material and the catalytic material, or a coating that may ameliorate adverse support/catalytic material interactions, or that may protect the support particles from attack in aggressive or unfavourable environments (for example, such as use or manufacture under adverse pH conditions that could otherwise cause dissolution of the support).

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows a schematic diagram of a catalyst in which a support particle is supported on a needle-shaped support particle.

Figure 2 shows a schematic diagram of a catalyst in which a catalytic material is supported on a spherical support particle;

Figure 3 shows a schematic diagram showing a mixture of the catalyst particles shown schematically in Figure 1;

Figure 4 shows a schematic diagram showing a mixture of the catalyst

particles shown schematically in Figure 2;

Figures 5 and 6 show TEM micrographs of the material of example 1 after exposure to a temperature of 1000°C for 2 hours;

Figure 7 shows a TEM micrograph of the material of example 2 following exposure to a temperature of 1000°C for 2 hours;

Figure 8 shows X-ray diffraction patterns comparing the materials from example 1 and comparative example 2; and

Figure 9 shows a TEM photomicrograph of plate-shaped boehmite nanoparticles suitable for use in some embodiments of the present invention.

DETAILED DESCRIPTION OF THE DRAWINGS

Figure 1 shows a schematic diagram of a catalyst in which a support particle is supported on a needle-shaped support particle. This schematic diagram shows a catalyst in accordance with an embodiment of the present invention. In Figure 1, the catalyst 1 comprises a support particle 2 and an island of catalytic material 3 supported thereon. The support particle may, for example be aluminium hydroxide needles, such as the needles available from SASOL GmbH under the DISPAL X-O trade mark. The support particles may also be alumina needles formed from aluminium hydroxide needles via heat treatment.

Figure 2 shows a schematic diagram of a catalyst in which a catalytic material is supported on a spherical support particle. This catalyst is representative of prior art catalysts. In figure 2, the catalyst 5 comprises a spherical particle 6 having an island 7 of catalytic material supported thereon.

To demonstrate the advantages of the present invention, some theoretical calculations have been conducted in respect of the catalysts schematically represented in Figures 1 and 2. For the catalyst of Figure 1, the support particle may be modelled as a cylinder having a diameter of 10nm and a length of 100nm.

The volume of the support particle is calculated from:

$V=\pi r^2 l$

Where r= radius of the cylinder and l=length of the cylinder.

The surface area of the support particle is calculated by first making the assumption that the support particle has no pores. This is an artificial assumption in that all support particles are likely to have at least some porosity and indeed, improved catalytic properties are likely to follow from using a porous support. However, for the

purposes of demonstrating the concept behind the present invention, it is only the external surface area that needs to be considered. For a cylinder, the external surface area (i.e. calculated without considering any pores in the support particle) is calculated by:

$$SA = 2(\pi r^2) + 2\pi rl$$

Where r = radius of the cylinder and l = length of the cylinder. The first term in the above equation represents the surface areas of the end faces of the cylinder and the second term in the above equation represents the surface area of the side wall of the cylinder.

The island of catalytic material can be modelled as a hemisphere having a diameter of 10nm (i.e. a radius of 5nm). The volume of this island is half the volume of a sphere of the same radius and the surface area of this island is half the surface area of a sphere of the same radius. The relevant equations are as follows:

$$V = (4/3\pi r^3)/2$$

$$SA = (4\pi r^2)/2$$

For the catalyst particle shown in Figure 1, the calculations mentioned above result in the following:

Volume of support particle = $7850nm^3$

Surface area of support particle = $3299nm^2$.

Volume of catalytic island = $261nm^3$

Surface area of catalytic island = $157nm^2$.

Thus, for the catalyst shown in Figure 1:

Volume fraction of catalytic island, as a percentage of the total volume of island plus support particle = 3.2%

Ratio of surface area of support particle to diameter of island of catalytic material = 21.

Ratio of length of support particle (maximum dimension) to diameter of catalytic island (maximum dimension) = 10.

For the catalyst shown schematically in Figure 2, which utilises a spherical support particle, it was desired to model a catalyst that had the same volume as the catalyst support particle shown in Figure 1. For a spherical particle having a volume of $7850nm^3$ (the volume of the support particle shown in Figure 1), the

spherical support particle will have a radius of about 12.3nm. The external surface area of such a support particle (again, assuming zero porosity) is 1901nm^2. The island of catalytic material supported on this support particle has the same dimensions as the island of catalytic material shown in Figure 1 (i.e. 10nm diameter, volume of 261nm^3, surface area of 157nm^2). Thus, for the catalyst shown in Figure 2:

Volume fraction of catalytic island, as a percentage of the total volume of island plus support particle = 3.2% (same as for the catalyst of Figure 1)

Ratio of surface area of support particle to diameter of island of catalytic material = 12 (compared to 21 for Figure 1).

Ratio of length of support particle (maximum dimension) to diameter of catalytic island (maximum dimension) = 2.45 (compared to 10 for Figure 1).

Thus, the catalyst of Figure 1, for a given volume fraction of catalytic material, has a higher ratio of surface area of support to surface area of catalytic island (assuming zero porosity) and a significantly higher ratio of length of support particle to diameter (or length or width) of catalytic island. Consequently, for a given catalytic material loading on the support particle at a given catalytic island size, the catalyst in accordance with the present invention has greater support surface area and greater support particle length. As a result, the islands of catalytic material are likely to be more isolated, or likely to have greater separation, from other islands of catalytic material than for prior art catalysts. Effectively, there is more likely to be greater separation between the catalytic islands in catalysts of the present invention, meaning that the adverse effects caused by diffusion and/or aggregation of the catalytic islands at elevated temperatures are likely to be reduced. These adverse effects are believed to be caused by elevated temperature leading to diffusion effects relating to the catalytic material on the support reducing the surface area of the catalytic material. In catalysts in accordance with the present invention, the greater spacing between the islands of catalytic material reduces those diffusion effects or delays the onset of those diffusion effects until a higher temperature has been reached.

It will be appreciated that Figures 1 and 2 show single particles of the catalyst. In use, a large number of catalysts will be used together. Thus, the catalyst for use will typically comprise a bulk mixture of catalyst particles. The packing arrangements of the catalyst particles in accordance with the present invention and the distribution of the islands or particles of catalytic material supported on the support

particles, also means that there is a much lower likelihood of an island or particle of catalytic material on any one particle lying close to an island or particle of catalytic material supported on an adjacent support particle in the bulk mixture of supported catalyst. Figures 3 and 4 show an example of this effect. Figure 3 shows a schematic diagram of a bulk mixture of the catalyst shown in Figure 1, whilst Figure 4 shows a schematic diagram of a bulk mixture of catalyst particles shown in Figure 2. As can be seen from Figures 3 and 4, a bulk mixture of the catalyst particles of Figure 1 has a much lower number of islands of catalytic material on a particle being located in close physical proximity to islands of catalytic material on other particles than for the bulk mixture of particles shown schematically in Figure 4. As the likelihood of diffusion and growth of the catalytic islands at elevated temperature increases with the number of islands of catalytic material located in close proximity to each other, the bulk mixture shown in Figure 3 will have lower loss of catalytic activity at elevated temperature than the bulk mixture shown in Figure 4.

The present inventors have also surprisingly found that using support particles in the form of plates or platelets also results in desirable porosity and surface areas being obtained. Intuitively, it would be expected that using plates as support particles would result in stacking of the plates to result in low porosity. Surprisingly, the plates do not tend to stack but rather lie at angles to each other to maintain good porosity.

The present invention allows for enhanced temperature stability of the catalyst for given catalyst loadings, or increased catalytic material loadings for similar temperature stability properties when compared to prior art catalysts.

EXAMPLES

Example 1.

15wt% CeO_2 on alumina was prepared. 11g cerium nitrate hexahydrate was dissolved in ~200g water. 27g boehmite needles (Sasol, Dispal X-O) were mixed into the solution using a high-speed mixer together with an additional 100g water. The needles were of average length of about 100nm, although some were longer than that. 32g of carbon black (Columbia Raven 850) was dispersed in the solution also using a high-speed mixer. 70g of surfactant (Erunon LA4) was added and mixed. This final

mixture was heated slowly to a temperature of 500°C, and then higher temperature testing was carried out for 2h at 1000°C.

Figures 5 and 6 are TEM micrographs of the material after 1000°C. Isolated particles of CeO_2 are present on needles of alumina.

Example 2.

A composition 15wt% $Ce_{0.537}Zr_{0.375}La_{0.025}Pr_{0.063}O_x$ on alumina was prepared in a similar manner to example 1, except that no carbon black was used. Cerium nitrate hexahydrate, zirconium carbonate, lanthanum nitrate hexahydrate and praseodymium nitrate hexahydrate were dissolved in the appropriate proportions to make 4.5 g of $Ce_{0.537}Zr_{0.375}La_{0.025}Pr_{0.063}O_x$, in ~15g water. 27g of boehmite needles (Sasol, Dispal X-O) was suspended in 100g water. The salt solution was added to the boehmite dispersion and mixed with a high-speed stirrer. 70g of surfactant (Erunon LA4) was added and mixed. This final mixture was heated slowly to a temperature of 500°C, and then higher temperature testing was carried out for 2h at 1000°C.

A TEM micrograph showing small, isolated second phase particles (arrowed) on an alumina needle is shown in figure 7.

Comparative example 1.

A Ce-Zr-La-Pr composition, similar to example 2, was prepared according to the methods outlined in patent. This material was heat treated similarly to example 2, including 2h at 1000°C to test thermal stability.

An x-ray diffraction (XRD) pattern (Co radiation) of the materials prepared in comparative example 1 and example 2 are compared in figure 4. Peaks from the ceria-containing phase are present in both patterns, and additionally the pattern from example 2 contains extra peaks from alumina.

In XRD, the grain size is indicated by the ratio of the peak height to peak width, or more accurately the full-width at half maximum height (FWHM). Larger grains give higher peak-to-width ratios, i.e. smaller FWHMs.

In figure 8, the main peak from the ceria-containing phase in material from example 2 is much shorter and wider compared to the corresponding peak from material made in comparative example 1. FWHMs for the peaks are 1.49 and 0.742

respectively. This clearly shows that grain growth at 1000°C was severely inhibited in the material prepared according to the present invention.

Example 3.

A composition 20 wt% $Ce_{0.53}Zr_{0.37}Pr_{0.06}La_{0.04}O_x$ on alumina was prepared in a similar manner to example 2, except that 16g of carbon black (Raven 850, Colombian Chemicals) was added to the solution/boehmite mix prior to high speed stirring.

Following the heat treatment to 1000°C, XRD showed a ceria-containing phase and alumina, TEM showed the structure consisted of nano-sized particles of the catalyst phase dispersed over needles of alumina. The surface area was 106 m^2/g, and the pore volume for pores between 10nm and ~200nm was 0.92cc/g.

Example 4.

A composition 20 wt% $Ce_{0.53}Zr_{0.37}Pr_{0.06}La_{0.04}O_x$ on alumina was prepared in a similar manner to example 3, except that an additional 1wt% Pd was included in the solution and no carbon black was added. Following the heat treatment to 1000°C, XRD showed a ceria-containing phase and alumina, TEM showed the structure consisted of nano-sized particles of the catalyst phase dispersed over needles of alumina. The surface area was 103 m^2/g, and the pore volume for pores between 10nm and ~200nm was 0.94cc/g.

Example 5.

A composition 20 wt% $Ce_{0.53}Zr_{0.37}Pr_{0.06}La_{0.04}O_x$ on alumina was prepared in a similar manner to example 3, except that polyethylene glycol (molecular weight ~ 400) was used in place of Erunon LA4. Following the heat treatment to 1000°C, XRD showed a ceria-containing phase and alumina. The surface area was 108 m^2/g, and the pore volume for pores between 10nm and ~200nm was 0.86cc/g.

Example 6.

A composition 20 wt% $Ce_{0.53}Zr_{0.37}Pr_{0.06}La_{0.04}O_x$ on alumina was prepared in a similar manner to example 3, except that citric acid was used in place of Erunon LA4. This is an example using a 'polymerised complex' method. Following

the heat treatment to 1000°C, XRD showed a ceria-containing phase and alumina, and TEM showed the structure consisted of nano-sized particles of the catalyst phase dispersed over needles of alumina. The surface area was ??m^2/g, and the pore volume for pores between 10nm and ~200nm was ??/g.

Example 7.

A composition 20 wt% $Ce_{0.53}Zr_{0.37}Pr_{0.06}La_{0.04}O_x$ on alumina was prepared via a hydrothermal method. 21.6 g of boehmite needles was dispersed in 250mls water. 7.55g cerium (IV) ammonium nitrate, 0.65g praseodymium nitrate hexahydrate, 0.5g lanthanum nitrate hexahydrate, and 2.93 zirconium carbonate was dissolved in 15mls water and 5g nitric acid (70% solution). This was added to the boehmite solution and then a further 300mls water added. The mixture was stirred overnight at ~90°C. 150g of ammonia was then added and the resulting precipitants filtered. These were heat treated similarly to the previous examples. Following the heat treatment to 1000°C, XRD showed a ceria-containing phase and alumina, TEM showed the structure consisted of nano-sized particles of the catalyst phase dispersed over needles of alumina, although the dispersion did not appear quite as good as previous examples. The surface area was 99m^2/g, and the pore volume for pores between 10nm and ~200nm was 0.53/g.

Example 8.

A composition 20 wt% $Ce_{0.53}Zr_{0.37}Pr_{0.06}La_{0.04}O_x$ on alumina was prepared via a co-precipitation route. A Ce-Zr-Pr-La solution with Dispal X-O needles was prepared in the same manner as example 3. 400mls ammonia solution was added rapidly to this mixture. The resulting precipitates were washed and filtered, then heat treated to 1000°C. XRD showed a ceria-containing phase and alumina, and the peak widths were similar to previous examples, indicating similar grain sizes.

Example 9

A composition 20wt% $Ce_{0.537}Zr_{0.375}La_{0.025}Pr_{0.063}O_x$ on alumina was prepared in a similar manner to example 1, except that no carbon black was used. Cerium nitrate hexahydrate, zirconium carbonate, lanthanum nitrate hexahydrate and praseodymium nitrate hexahydrate were dissolved in the appropriate proportions to

make 4 g of $Ce_{0.537}Zr_{0.375}La_{0.025}Pr_{0.063}O_x$, in ~15g water. 21.6g of boehmite needles was dispersed in 300g water. The salt solution was added to the boehmite dispersion and mixed with a high-speed stirrer. 70g of surfactant (Erunon LA4) was added and mixed. This final mixture was heated slowly to a temperature of 500°C. The surface area was 217 m^2/g, and the pore volume for pores between 10nm and ~200nm was 0.34 cc/g.

Comparative example.

The same material in example was prepared in an identical manner, except that the salt solution was diluted with 82g water prior to addition to the dispersion. This raised the pH of the solution prior to contact with the needle dispersion.

Following the heat treatment to 500°C, the surface area was 213 m^2/g, and the pore volume for pores between 10nm and ~200nm was 0.6 cc/g. Clearly diluting the solution prior to contact with the dispersion was beneficial to the pores, even though the final solution conditions were similar. The inventors believe this is due to the lower pH in the first case causing agglomeration of particles that was not completely diminished by subsequent dispersion.

Example 10.

Using methods similar to the previous examples, NiO on alumina was prepared in a ratio corresponding to 20wt% Ni on alumina. Following heat treatment to 500°C, the surface area was 183 m^2/g, and the pore volume for pores between 10nm and ~200nm was 0.65 cc/g.

Example 11.

Using methods similar to the previous examples, CuO on alumina was prepared in a ratio corresponding to 20wt% Cu on alumina. Following heat treatment to 500°C, the surface area was 181 m^2/g and the pore volume for pores between ~2nm and ~200nm was 0.4cc/g.

Example 12

A composition 20 wt% $Ce_{0.53}Zr_{0.37}Pr_{0.06}La_{0.04}O_x$ on alumina was prepared in a similar manner to example 1, except that DISPAL 18HP was used

instead of X-O.

Following the heat treatment to 1000°C, XRD showed a ceria-containing phase and alumina. TEM showed the structure consisted of nano-sized particles of the catalyst phase dispersed throughout the alumina. The surface area was 85.7 m^2/g, and the pore volume for pores between 2nm and ~200nm was 0.66 cc/g.

Example 13

A composition 20wt% Cu on alumina was prepared by first dispersing 13.97g of DISPAL 23N4-80 plate-shaped boehmite nanoparticles in 200mls water. A TEM photomicrograph of the plate-shaped boehmite nanoparticles is shown in Figure 9.

68.18g of a 50.2wt% Cu(NO3)2.3H2O solution and 200mls water was then added to the dispersion. 47g of LA4 surfactant was added, and the mix slowly heated to 500°C. XRD showed CuO on alumina. The surface area was 121 m^2/g, and the pore volume for pores between 2nm and ~200nm was 0.45 cc/g.

Those skilled in the art will appreciate that the present invention may be subject to variations and modifications other than those specifically described. It is to be understood that the present invention encompasses all such variations and modifications that fall within its spirit and scope.

Claims.

1. A catalyst comprising a catalytic material supported on a support, characterised in that the support comprises particles predominantly having a maximum particle size of less than 1000nm and an aspect ratio of greater than 2, and the catalytic material is mainly present in the form of discrete islands of catalytic material supported on the support, with a substantial proportion of the islands of catalytic material being separate and isolated from other islands of catalytic material.
2. A catalyst as claimed in claim 1 wherein the islands of catalytic material are separate and isolated from other islands of catalytic material such that diffusion and growth of the islands of catalytic material at elevated temperature is minimised or avoided.
3. A catalyst as claimed in claim 1 wherein the support material is in the form of needles, laths or platelets.
4. A catalyst as claimed in claim 1 wherein the support material has an aspect ratio of from 2-1000.
5. A catalyst as claimed in claim 1 wherein at least 50% of the islands of catalytic material (by number) are isolated and separate from other islands of catalytic material.
6. A catalyst as claimed in claim 5 wherein a substantial proportion of the support particles have only a single island of catalytic material supported thereon.
7. A catalyst as claimed in claim 6 wherein at least 50% of the support particles (by number) have only have a single island of catalytic material supported thereon.
8. A catalyst as claimed in claim 1 wherein the islands of catalytic material are sized such that a substantial proportion of the islands have a maximum diameter of less than 100nm.
9. A catalyst as claimed in claim 8 wherein the islands of catalytic material are sized such that a substantial proportion of the islands have a maximum diameter of less than 20nm.
10. A catalyst as claimed in claim 8 wherein at least 50% of the islands of catalytic material have a maximum diameter of less than 100nm.
11. A catalyst as claimed in claim 1 wherein the volume percent of catalytic

material falls within the range of from about 1% to about 40%.

12. A catalyst as claimed in claim 12 wherein the volume percent of catalytic material falls within the range of from about 5% to about 20%.

13. A catalyst as claimed in claim 1 wherein the ratio of the length of the support particles to the width of the islands or particles of the catalytic material is at least 3:1.

14. A catalyst as claimed in claim 13 wherein the ratio of the length of the support particles to the width of the islands or particles of the catalytic material is from about 4:1 to about 100:1.

15. A catalyst as claimed in claim 1 wherein the support particles are branched particles.

16. A catalyst as claimed in claim 15 wherein the branched particles comprise a stable agglomeration of smaller platelet or needle particles having a branched structure.

17. A catalyst as claimed in claim 1 wherein the ratio of surface area of support particles (calculated as if the support particles have zero porosity) to surface area of catalytic material is at least 2:1.

18. A catalyst as claimed in claim 17 wherein the ratio of surface area of support particles (calculated as if the support particles have zero porosity) to surface area of catalytic material falls within the range of about 2:1 to about 100:1.

19. A catalyst comprising a catalytic material supported on support particles, characterised in that the catalytic material is present at a volume percent of at least 1%, by volume of the catalyst, that the catalytic material is present in the form of discrete islands or particles on the support particles, and that the ratio of the length of the support particles to the width of the islands or particles of the catalytic material is at least 3:1.

20. A catalyst as claimed in claim 19 wherein the islands of catalytic material are separate and isolated from other islands of catalytic material such that diffusion and growth of the islands of catalytic material at elevated temperature is minimised or avoided.

21. A catalyst as claimed in claim 19 wherein the support material is in the form of needles, laths or platelets.

22. A catalyst as claimed in claim 19 wherein the support material has an aspect

ratio of from 2-1000.

23. A catalyst as claimed in claim 19 wherein at least 50% of the islands of catalytic material (by number) are isolated and separate from other islands of catalytic material.

24. A catalyst as claimed in claim 24 wherein a substantial proportion of the support particles have only a single island of catalytic material supported thereon.

25. A catalyst as claimed in claim 25 wherein at least 50% of the support particles (by number) have only have a single island of catalytic material supported thereon.

26. A catalyst as claimed in claim 19 wherein the islands of catalytic material are sized such that a substantial proportion of the islands have a maximum diameter of less than 100nm.

27. A catalyst as claimed in claim 26 wherein the islands of catalytic material are sized such that a substantial proportion of the islands have a maximum diameter of less than 20nm.

28. A catalyst as claimed in claim 28 wherein at least 50% of the islands of catalytic material have a maximum diameter of less than 100nm.

29. A catalyst as claimed in claim 19 wherein the volume percent of catalytic material falls within the range of from about 1% to about 40%.

30. A catalyst as claimed in claim 12 wherein the volume percent of catalytic material falls within the range of from about 5% to about 20%.

31. A catalyst as claimed in claim 19 wherein the ratio of the length of the support particles to the width of the islands or particles of the catalytic material is from about 4:1 to about 100:1.

32. A catalyst as claimed in claim 19 wherein the support particles are branched particles.

33. A catalyst as claimed in claim 32 wherein the branched particles comprise a stable agglomeration of smaller platelet or needle particles having a branched structure.

34. A catalyst as claimed in claim 19 wherein the ratio of surface area of support particles (calculated as if the support particles have zero porosity) to surface area of catalytic material is at least 2:1.

35. A catalyst as claimed in claim 17 wherein the ratio of surface area of support particles (calculated as if the support particles have zero porosity) to surface area of catalytic material falls within the range of about 2:1 to about 100:1.

36. A catalyst comprising a catalytic material supported on support particles, characterised in that a ratio of surface area of support particles (calculated as if the support particles have zero porosity) to surface area of catalytic material is at least 2:1 and the catalytic material is present at a volume percent of at least 1%, by volume of the catalyst.

37. A catalyst as claimed in claim 36 wherein the islands of catalytic material are separate and isolated from other islands of catalytic material such that diffusion and growth of the islands of catalytic material at elevated temperature is minimised or avoided.

38. A catalyst as claimed in claim 36 wherein the support material is in the form of needles, laths or platelets.

39. A catalyst as claimed in claim 36 wherein the support material has an aspect ratio of from 2-1000.

40. A catalyst as claimed in claim 36 wherein at least 50% of the islands of catalytic material (by number) are isolated and separate from other islands of catalytic material.

41. A catalyst as claimed in claim 40 wherein a substantial proportion of the support particles have only a single island of catalytic material supported thereon.

42. A catalyst as claimed in claim 41 wherein at least 50% of the support particles (by number) have only have a single island of catalytic material supported thereon.

43. A catalyst as claimed in claim 36 wherein the islands of catalytic material are sized such that a substantial proportion of the islands have a maximum diameter of less than 100nm.

44. A catalyst as claimed in claim 43 wherein the islands of catalytic material are sized such that a substantial proportion of the islands have a maximum diameter of less than 20nm.

45. A catalyst as claimed in claim 8 wherein at least 50% of the islands of catalytic material have a maximum diameter of less than 100nm.

46. A catalyst as claimed in claim 36 wherein the volume percent of catalytic material falls within the range of from about 1% to about 40%.

47. A catalyst as claimed in claim 46 wherein the volume percent of catalytic material falls within the range of from about 5% to about 20%.

48. A catalyst as claimed in claim 36 wherein the ratio of the length of the support particles to the width of the islands or particles of the catalytic material is at least 3:1.

49. A catalyst as claimed in claim 48 wherein the ratio of the length of the support particles to the width of the islands or particles of the catalytic material is from about 4:1 to about 100:1.

50. A catalyst as claimed in claim 36 wherein the support particles are branched particles.

51. A catalyst as claimed in claim 50 wherein the branched particles comprise a stable agglomeration of smaller platelet or needle particles having a branched structure.

52. A catalyst as claimed in claim 36 wherein the ratio of surface area of support particles (calculated as if the support particles have zero porosity) to surface area of catalytic material falls within the range of about 2:1 to about 100:1.

53. A catalyst comprising a catalytic material supported on support particles, characterised in that the catalytic material is present in the form of discrete islands of material supported on the support particles and a substantial proportion of the support particles have only a single island of catalytic material thereon.

54. A catalyst as claimed in claim 53 wherein the islands of catalytic material are separate and isolated from other islands of catalytic material such that diffusion and growth of the islands of catalytic material at elevated temperature is minimised or avoided.

55. A catalyst as claimed in claim 53 wherein the support material is in the form of needles, laths or platelets.

56. A catalyst as claimed in claim 53 wherein the support material has an aspect ratio of from 2-1000.

57. A catalyst as claimed in claim 53 wherein at least 50% of the support particles (by number) have only have a single island of catalytic material supported

thereon.

58. A catalyst as claimed in claim 53 wherein the islands of catalytic material are sized such that a substantial proportion of the islands have a maximum diameter of less than 100nm.

59. A catalyst as claimed in claim 58 wherein the islands of catalytic material are sized such that a substantial proportion of the islands have a maximum diameter of less than 20nm.

60. A catalyst as claimed in claim 58 wherein at least 50% of the islands of catalytic material have a maximum diameter of less than 100nm.

61. A catalyst as claimed in claim 53 wherein the volume percent of catalytic material falls within the range of from about 1% to about 40%.

62. A catalyst as claimed in claim 61 wherein the volume percent of catalytic material falls within the range of from about 5% to about 20%.

63. A catalyst as claimed in claim 53 wherein the ratio of the length of the support particles to the width of the islands or particles of the catalytic material is at least 3:1.

64. A catalyst as claimed in claim 63 wherein the ratio of the length of the support particles to the width of the islands or particles of the catalytic material is from about 4:1 to about 100:1.

65. A catalyst as claimed in claim 53 wherein the support particles are branched particles.

66. A catalyst as claimed in claim 65 wherein the branched particles comprise a stable agglomeration of smaller platelet or needle particles having a branched structure.

67. A catalyst as claimed in claim 53 wherein the ratio of surface area of support particles (calculated as if the support particles have zero porosity) to surface area of catalytic material is at least 2:1.

68. A catalyst as claimed in claim 67 wherein the ratio of surface area of support particles (calculated as if the support particles have zero porosity) to surface area of catalytic material falls within the range of about 2:1 to about 100:1.

69. A catalyst as claimed in claim 1 wherein the support particles comprise support materials selected from the group consisting of metal oxides, mixed metal oxides, silicate materials, carbon-based materials, polymeric materials, clay

materials, zeolites, layered double hydroxide materials and mixtures thereof.

70. A catalyst as claimed in claim 1 wherein the catalytic material is selected from the group consisting of noble metals, platinum group metals, catalytically active metals, oxides of catalytically active metals, mixed metal oxides, complex metal oxides, perovskites and mixtures thereof.

71. A catalyst as claimed in claim 1 wherein the catalyst comprises a bulk mixture of the individual particles of the catalyst.

72. A catalyst as claimed in claim 1 wherein the catalyst comprises catalyst particles supported on a larger support.

73. A catalyst as claimed in claim 72 wherein the larger support is a monolith, a honeycomb support, or macroscopic particles.

74. A catalyst as claimed in claim 1 wherein the catalyst particles are bonded together to make larger particles or tablets or shapes.

75. A method for preparing a catalyst including preparing a mixture of support particles predominantly having a maximum particle size of less than 1000nm and an aspect ratio of greater than 2 with one or more precursors of a catalytic material and treating the mixture to form a catalyst in which the catalytic material is mainly present in the form of discrete islands of catalytic material supported on the support particles, with a substantial proportion of the islands of catalytic material being separate and isolated from other islands of catalytic material such that diffusion and growth of the islands of catalytic material at elevated temperature is minimised or avoided.

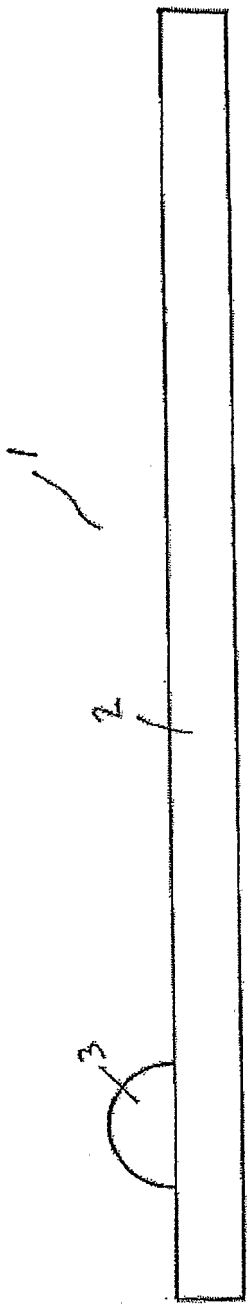

Figure 1.

Figure 2

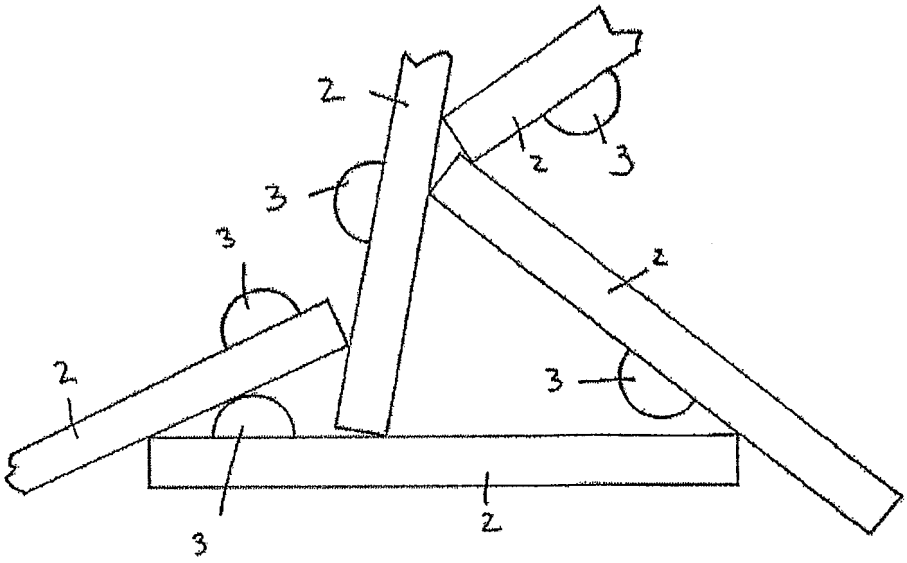

FIGURE 3

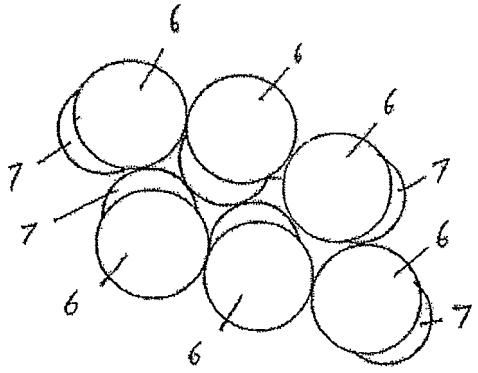

FIGURE 4

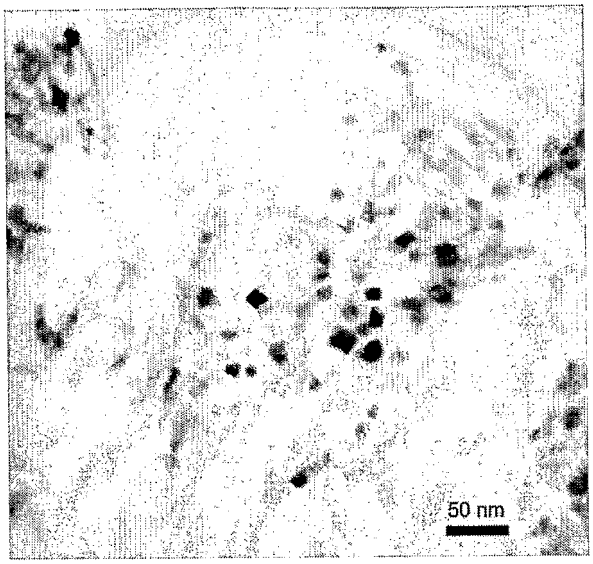

Figure 5

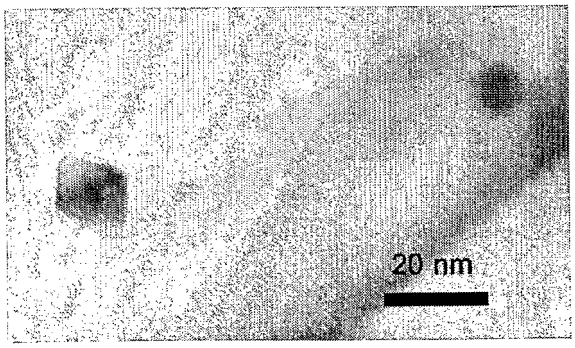

Figure 6

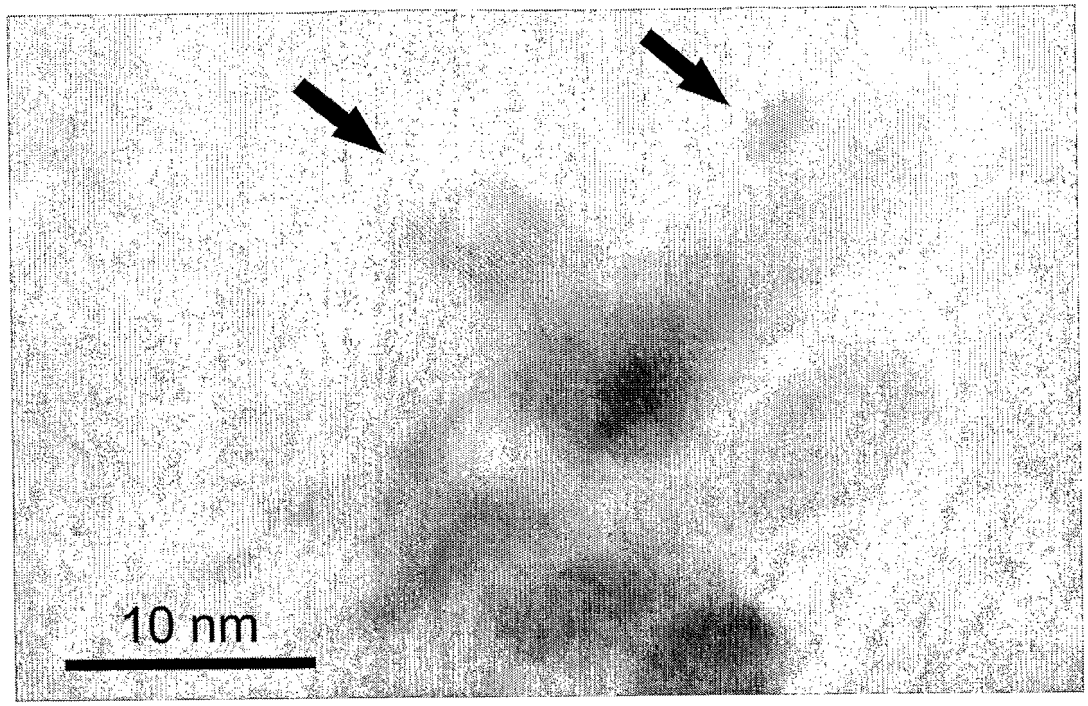

Figure 7

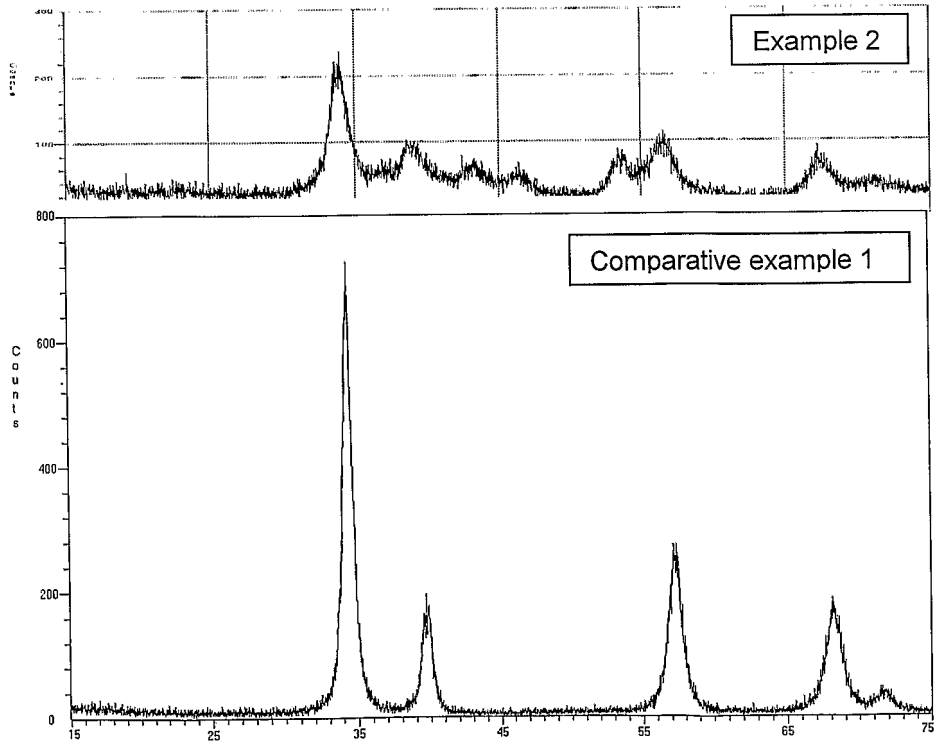

Figure 8

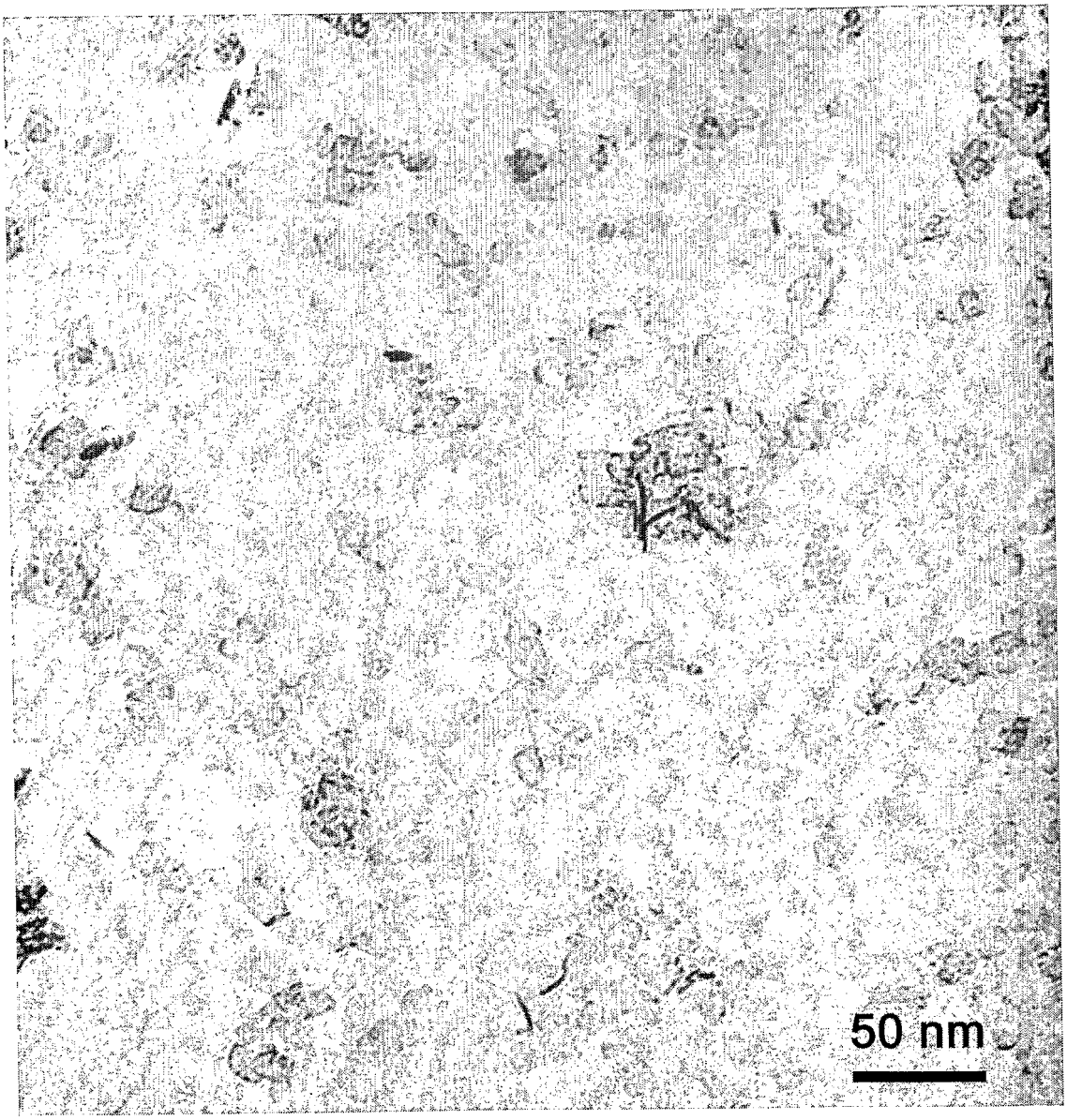

Figure 9

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU2006/000596

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl.

B01J 32/00 (2006.01) ***B01J 23/00*** (2006.01) ***B01J 37/02*** (2006.01)
B01J 21/00 (2006.01) ***B01J 35/02*** (2006.01)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
DWPI: B01J 32/IC, 35/00/IC, 35/02, 35/04, 35/06, 35/08, 35/10 & keywords: island+ or zones or areas or regions or discrete, particle+, nano+, catalyst support+, particle support+

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	US 2005/0159306 A1 (KEZUKA et. al.) 21 July 2005 Whole document and in particular [0057]-[0058], [0060]-[0061]	1-2, 4-5
X	WO 2000/041808 A1 (HYPERION CATALYSIS INTERNATIONAL INC) 20 July 2000 Whole document and in particular pages 11, 17, 28-29, 39-41, 43, Figs., claims	1-75
X	WO 2003/055583 A2 (HYPERION CATALYSIS INTERNATIONAL INC) 10 July 2003 Whole document and in particular pages 9, 13-14, 23, 35, 48, Table 2, Figs., claims	1-75

[X] Further documents are listed in the continuation of Box C [X] See patent family annex

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
19 June 2006	28 JUN 2006
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA E-mail address: pct@ipaustralia.gov.au Facsimile No. (02) 6285 3929	Authorized officer **Roger Howe** Telephone No : (02) 6283 2159

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU2006/000596

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5879827 A (DEBE et. al.) 9 March 1999 Whole document and in particular column 4 lines 56-58, column 6 lines 54-56, column 14 lines 21-24	1-4, 69-70
X	US 2005/0070427 A1 (PAK) 31 March 2005 Whole document and in particular [0024]-[0027], [0028]	1-4, 69-70, 75
X	US 2004/0194705 A1 (DAI et. al.) 7 October 2004 Whole document and in particular abstract, Figs., [0050]	53-56
A	US 2005/0053826 A1 (WANG et. al.) 10 March 2005 Whole document	1-75
A	US 2004/0082178 A1 (KAMINS et. al.) 29 April 2004 Whole document and in particular [0022]-[0023], [0029] and Figs.	1-75
A	US 2003/0116503 A1 (WANG et. al.) 26 June 2003 Whole document and in particular [0004], [0073]	1-75
A	US 2004/0241445 A1 (YUDASAKA et. al.) 2 December 2004 Whole document	1-74

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU2006/000596

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a)

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:
This International Application does not comply with the requirements of unity of invention because it does not relate to one invention or to a group of inventions so linked as to form a single general inventive concept.

Continued on extra sheet.

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☒ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

Supplemental Box
(To be used when the space in any of Boxes I to VIII is not sufficient)

Continuation of Box No: III

In assessing whether there is more than one invention claimed, I have given consideration to those features which can be considered to potentially distinguish the claimed combination of features from the prior art. Where different claims have different distinguishing features they define different inventions.

This International Searching Authority has found that there are different inventions as follows:

- Claims 1-16, 19-33, 45, 53-66, 69-75 are directed toward a catalyst comprising a catalytic material supported on a support, characterised in that the catalytic material is mainly present in the form of discrete islands of catalytic material supported on the support. It is considered that "catalytic material is mainly present in the form of discrete islands" comprises a first distinguishing feature.

- Claims 36, 38-44, 46-52, and 67-68 are directed to a catalyst comprising a catalytic material supported on support particles, characterised in that a ratio of surface area of support particles (calculated as if the support particles have zero porosity) to surface area of catalytic material is at least 2:1. It is considered that "surface area of support particles (calculated as if the support particles have zero porosity) to surface area of catalytic material is at least 2:1" comprises a second distinguishing feature.

Claims 17-18, 34-35, 37, and 67-68 are dependent claims and have both special technical features.

PCT Rule 13.2, first sentence, states that unity of invention is only fulfilled when there is a technical relationship among the claimed inventions involving one or more of the same or corresponding special technical features. PCT Rule 13.2, second sentence, defines a special technical feature as a feature which makes a contribution over the prior art.

Each of the abovementioned groups of claims has a different distinguishing feature and they do not share any feature which could satisfy the requirement for being a special technical feature. Because there is no common special technical feature it follows that there is no technical relationship between the identified inventions. Therefore the claims do not satisfy the requirement of unity of invention *a priori*.

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member					
US	2005159306	JP	2005199204				
WO	0041808	AU	11868/01	AU	25040/00	AU	2002365183
		CA	2359336	CA	2396922	CA	2465002
		CN	1607979	EP	1152827	EP	1246695
		EP	1448295	MX	PA02006763	MX	PA04003998
		US	6514897	US	6809229	US	6841508
		US	6936565	US	2002121460	US	2003008772
		US	2003035769	US	2005027153	US	2005029164
		WO	0151201	WO	03055583		
US	5879827	AU	74696/98	CA	2304157	CN	1278747
		EP	1021246	US	6040077	WO	9919066
US	2005070427	CN	1645655	JP	2005108838		
US	2004194705	EP	1247089	US	6346189	US	6528020
		US	2002179434	US	2003049444	US	2003068432
		WO	0009443	WO	0144796		
US	2005053826	US	2005112450	WO	2005084399		
US	2004082178	AU	2003279914	EP	1556530	US	2004079278
		US	2005191774	WO	2004040049		
US	2003116503	AU	2002367020	CA	2470025	EP	1465836
		US	6713519	US	6824689	US	7008969
		US	7011760	US	2003119920	US	2004147620
		US	2005040090	WO	03059813		
US	2004241445	CN	1527794	EP	1413544	JP	2003025297
		WO	03006361				

Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.

END OF ANNEX